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EP 0 458 472 B1

Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to structures which can be used in reactions wherein the reaction and distillation of the reaction mixture are carried on concurrently using the structures as both catalyst for the reaction and as distillation structures. More particularly the present invention relates to a rigid container having distillation surfaces thereon, the container being filled with a particulate catalyst component.

Related Art

A new method of carrying out catalytic reactions has been developed, wherein the components of the reaction mixture are concurrently separable by fractional distillation. Several systems have been proposed and one commercially successful uses the catalyst as the catalytic distillation structure. Such a system is variously described in U.S. patents 4,215,011; 4,232,177; 4,242,530; 4,250,052; 4,302,356; 4,307,254; 4,336,407; 4,439,350; 4,443,559; and 4,482,775.

Briefly, the commercial structure described therein comprises a cloth belt with a plurality of pockets spaced along the belt and containing particulate catalyst material. The cloth belt with catalyst filled pockets is wound into a helix about a spacing material such as knitted stainless steel wire mesh, and these "bales" loaded into a distillation column. Additionally U.S. patents 4,443,559 and 4,250,052 disclose a variety of catalyst structures for this use.

Placing the particulate catalyst loose on standard distillation trays has also been proposed. See, for example, U.S. Pat. No. 4,215,011 and U.K. patents GB 2,096,603 and 2,096,604. The placement of the catalyst in the downcomers of standard distillation columns has been proposed as in U.S. patent 3,634,534. Fluidization of the catalyst on the trays has also been suggested as in U.S. patent 4,471,154. Some deficiencies of such fluidized beds were recognized in Chemiker Zeitung/Chemische Apparatur, vol. 90, no. 13, July 1966 and U.S. Pat. No. 4,215,011. Quang, et al, in U.S. Pat. No. 4,847,430 and Nocca, et al in U.S. Pat. No. 4,847,431 disclose loading the particulate catalyst on alternating trays of a distillation column and with a gas by pass about the catalyst loaded trays.

An alternative arrangement is described in US-A-4 536 373 where the catalyst is housed in porous containers which are supported on the distillation trays in a distillation column reactor.

So far, the most commercially successful arrangement has been to the place the particulate catalyst in closed pockets disposed along a fiber glass cloth belt.

The main problems sought to be overcome by the improvements have been the reduction of pressure drop through the column and provision of sufficient contact of the reactants with the catalyst while providing for good vapor liquid contact for the fractional distillation. Many useful catalysts are in the form of fine particulate powders which preclude their use directly as distillation components. Even larger extruded pellets do not lend themselves well as distillation structures. Hence the use of cloth belts, cages and support trays. While larger catalysts structures have been proposed, the porosity requirements of many catalytic materials limit their structural integrity. Many catalysts which rely on outer surface activity only and which might have the strength for larger structures are useful only for gas phase reactions, such as maleic anhydride production.

SUMMARY OF THE INVENTION

The present invention provides catalytic distillation structures which are useful in the concurrent reaction and distillation of a reaction mixture. The distillation structures are provided as small rigid containers. The catalyst component is loaded into the containers and the containers closed off. Although the containers are closed off, openings are provided to allow vapor and liquid passage into and out of the containers. A multitude of catalyst containers are placed into a distillation column which then becomes a reactor/distillation column. The surfaces of the containers provide the necessary vapor/liquid contact surfaces for the distillation. The rigidity of the containers provides for spacing the structures and the necessary free space for the distillation.

In particular, the present invention relates to a catalytic distillation structure for use as packing material in a distillation column reactor, comprising a particulate catalyst component disposed in a rigid container having openings thereon to allow free passage of liquid and vapours, the container surfaces providing the distillation contact surfaces, said container being substantially smaller in volume than said distillation column reactor volume.

In one embodiment of this invention, the rigid container of the catalytic distillation structure referred to above comprises a hollow cylinder closed at both ends and having openings in the ends and wall to allow liquid and vapour to enter and leave said container, both the length and diameter of the hollow cylinder are substantially smaller than the

corresponding dimensions of the distillation column reactor.

In a second embodiment of this invention, the rigid container comprises a hollow cylinder having an inner wall extending generally parallel to the cylindrical wall of the cylinder and having the ends closed to divide the space within the cylinder into a hollow central space which is open at both ends and a second space surrounding the central space which is closed at both ends. The catalyst component is disposed in the second closed space. This second space has openings in the ends and walls which allow liquid and vapour to enter and leave the space. Both the length and diameter of the container are substantially smaller than the corresponding dimensions of the distillation column reactor.

In a third embodiment of the present invention, the rigid container comprises a hollow cylinder which is closed at both ends and which has an inner wall extending generally parallel to the cylindrical wall of the cylinder dividing the space within the cylinder into a closed central space and a second closed space surrounding said central space, said catalyst component being disposed in said central space and said ends and walls having openings to allow liquid and vapour to pass through said second space and pass into and out of said central space.

In each of these embodiments, the openings may comprise circular ports in the ends and wall or walls of the rigid container. In one alternative arrangement, the openings may comprise circular ports in the ends and longitudinally slotted ports in the wall or walls of the rigid container. In one preferred arrangement, a longitudinal fin extends radially from one side of each of said slotted ports.

The openings, which may be covered with a porous material, are preferably smaller than the particles of the catalyst component. In one alternative arrangement, the Openings are larger than the parties of said catalyst component and the catalytic distillation structure further comprises a porous lining to retain the particles within the container.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a depiction of a cylindrical catalytic distillation structure container having circular openings in the ends and wall.

FIG. 2 is a depiction of a cylindrical catalytic distillation structure container having circular openings in the ends and longitudinal slotted openings in the wall.

FIG. 3 is a depiction of the cylindrical catalytic distillation structure container of FIG. 2 having radially extending fins along one side of each of the slotted openings.

FIG. 4 is a depiction of a cylindrical catalytic distillation structure container having circular openings in the ends and longitudinally spiralled slotted openings in the wall.

FIG. 5 is a depiction of an annular cylindrical catalytic distillation structure container wherein the catalyst component is disposed within the inner cylindrical space.

FIG. 6 is a depiction of an annular cylindrical catalytic distillation structure container wherein the catalyst component is disposed within the annular space.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides catalytic structures which can be used as distillation structures. In order to serve both functions there are three highly desirable criteria. First, the structure should be such as to provide for relatively even spatial dispersion in the distillation column reactor. That is, the catalyst structures rest in the column in a geometric arrangement which will perform the desired functions of reaction and distillation sites. To achieve this these structures may be such as to provide fairly uniform spatial distribution in the column.

A second criteria is that there be sufficient free space in the catalyst bed to allow for the liquid phase contact and vapor phase distillation with the concurrent separation of the material in the column by the distillation into vapor and liquid phases. It has been observed that in the catalyst bed a free space of about 50 volume percent is adequate to obtain operable fractionation.

A third criteria is for the catalyst bed to be able to expand and contract during use without undue attrition of the catalyst.

The criteria are met by providing rigid containers containing the catalyst component. The containers may be of convenient size and shape so as to resemble common distillation column packing such as pall rings, burls, saddles, etc. Most preferably the containers are cylindrical in shape and have a volume for containing the catalyst component of about 14.2 ml to 1818 ml (1/2 to 64 fluid ounces) The size of the containers is thus very small, e g. $1x10^{-7}$ to $7x10^{-5}$ the volume of conventional distillation column reactors into which they are placed.

The walls and/or ends of the cylindrical containers are provided with openings to allow the liquid and vapor to contact the catalyst component for reaction. The surfaces of the containers provide the distillation surface for gas/vapor contact.

Depending upon the size of the particulate catalyst, the openings may be sized to prevent the particles from escaping the container. Extremely fine catalytic materials might be contained within the cylinders by a porous liner. Even with the liner, the advantages of the rigidity of the catalytic structure is retained with the distillation surfaces exposed.

The volume of the catalyst loaded into the containers will depend upon its reaction to wetting. One common acidic ion exchange resin used -- Amberlyst 15 -- swells up to 20-30 percent upon wetting, while another -- CT-175 -- swells only 10 to 15 percent. Crystalline zeolites swell hardly at all upon wetting.

The uniformity and spatial relationship will depend upon the size of the containers and the loading procedure used. A typical 14.2 ml (1/2 fluid ounce) cylindrical container is about 38.1 mm (1½ inches) by 19.1 mm (3/4 inch) -- a L/D ratio of 2. Such containers could be randomly poured into a column like standard distillation packing and would be expected to provide the necessary spatial relationship and free space. Larger containers (1818 ml (64 fluid ounces)) might require hand loading of individual containers to assure even spacing with the required free space. While other geometrical shapes for the containers are contemplated to be covered, manufacture and filling of cylindrical containers is expected to be more easily practiced.

Referring now to the figures, various embodiments of the present invention are shown. In figures 1-6 the container 10 of the catalytic distillation structure is shown to be substantially in the form of a hollow cylinder having openings in the ends 11 and wall 12 to allow free flow of liquid and vapor into and out of the container.

The cylindrical containers should be of a rigid material that is able to hold its integrity even with the openings. Additionally, the materials of construction of the container must be able to withstand the environment within a distillation column reactor. Any of the various grades of stainless steel or some of the newer plastics which are available would be suitable depending upon the service.

In FIGS. 1-4 the difference between the embodiments lies in the type of openings in the ends 11 or wall 12 of the cylindrical container. In FIG. 1 the openings in both the ends 11 and wall 12 are in the form of circular ports 14. In FIG. 2 the openings in the wall 12 are in the form of longitudinal slots 15. In FIG. 3 additional distillation surface is provided in the form of longitudinal fins 16 extending radially along one side of each slot 15. In FIG. 4 the openings in the wall 12 are in the form of longitudinally spiralled slots 17.

In FIGS. 5 and 6 an alternative embodiment of the rigid container 10 is shown. Essentially the container comprises two axially aligned cylinders with outer wall 12 and inner wall 20 defining an annular space. In FIG. 6 only the ends of the annular space are closed and the catalyst component is placed within this annular space 18. In FIG. 5 each entire end 11 is closed and the catalyst component is disposed in the inner cylindrical space 20. Any combination of the openings discussed above may be used with the cylindrical annular containers of FIG. 5 or FIG. 6.
In FIG. 5, moreover, an additional embodiment of the slotted opening arrangement is shown wherein the fins 16 extend radially inward along each slot.

If very small catalyst are used, then a porous filter or screen 22 may be inserted into the container to cover the openings.

An interesting feature of the present invention is that the opening may be preformed in the containers, i.e. before the catalysts is placed therein or the catalyst may be sealed in the containers just as food or other items are stored in cans and the perforations made just prior to loading the catalyst structure into the reactor distillation column. This is an excellent means to preserve and protect the catalyst for storage, i.e. so that a fully active backup charge may be stored without special precautions. This feature also provides a very safe form for transoceanic shipment.

The terms "Amberlyst 15" and "CT-175" are trade marks which may be registered in one or more of the territories designated in this application.

Claims

1. A catalytic distillation structure for use as packing material in a distillation column reactor, comprising a particulate catalyst component disposed in a rigid container having openings thereon to allow free passage of liquid and vapours, the container surfaces providing the distillation contact surfaces, said container being substantially smaller in volume than said distillation column reactor volume.

2. The catalytic distillation structure or claim 1 wherein said rigid container comprises a hollow cylinder closed at both ends and having openings in the ends and wall to allow liquid and vapor to enter and leave said container, both the length and diameter of said hollow cylinder being substantially smaller than the corresponding dimensions of said distillation

column reactor.

3. The catalytic distillation structure of claim 1 wherein said rigid container comprises a hollow cylinder having an inner wall extending generally parallel to the cylindrical wall of the cylinder and having the ends closed to divide the space within the cylinder into a hollow central space which is open at both ends and a second space surrounding the central space which is closed at both ends, said catalyst component being disposed in said second closed space, said second space having openings in the ends and walls to allow liquid and vapor to enter and leave said second space, both the length and diameter of said container being substantially smaller than the corresponding dimensions of said distillation column reactor.

4. The catalytic distillation structure of claim 1 wherein said rigid container comprises a hollow cylinder closed at both ends and having an inner wall extending generally parallel to the cylindrical wall of the cylinder dividing the space within the cylinder into a closed central space and a second closed space surrounding said central space, said catalyst component being disposed in said central space and said ends and walls having openings to allow liquid and vapor to pass through said second space and pass into and out of said central space.

5. The catalytic distillation structure of any one of claims 1 to 4 wherein said openings comprise circular ports in the ends and wall or walls of said rigid container.

6. The catalytic distillation structure of any one of claims 1 to 4 wherein said openings comprise circular ports in the ends and longitudinally slotted ports in the wall or walls of said rigid container.

7. The catalytic distillation structure of claim 6 further comprising a longitudinal fin extending radially from one side of each of said slotted ports.

8. The catalytic distillation structure of any one of claims 1 to 7 wherein said openings are smaller than the particles of said catalyst component.

9. The catalytic distillation structure of any one of claims 1 to 8 wherein said openings are covered with a porous material.

10. The catalytic distillation structure of any one of claims 1 to 7 wherein said openings are larger than the particles of said catalyst component and further comprising a porous lining to retain said particles within said container.

11. The catalytic distillation structure of any one of claims 1 to 10 wherein the catalyst capacity of said rigid container is between 14.2 to 1818 ml (1/2 to 64 fluid ounces).

Patentansprüche

1. Katalytische Destillationsstruktur zur Verwendung als Packmaterial in einem Reaktor in Form einer Destillationskolonne, umfassend eine partikuläre Katalysatorkomponente, die in einem starren Behälter angeordnet ist, auf dem sich Öffnungen für den freien Durchtritt von Flüssigkeit und Dämpfen befinden, wobei die Oberflächen des Behälters die Destillationskontaktoberflächen darstellen und wobei das Volumen des Behälters erheblich kleiner ist als das Volumen des Destillationskolonnenreaktors.

2. Katalytische Destillationsstruktur nach Anspruch 1, in der der starre Behälter einen Hohlzylinder umfaßt, der an beiden Enden geschlossen ist und an den Enden und in der Wand Öffnungen für den Ein- und Austritt von Flüssigkeit und Dampf in diesen Behälter aufweist, wobei sowohl die Länge als auch der Durchmesser des Hohlzylinders erheblich kleiner ist als die entsprechenden Abmessungen des Destillationskolonnenreaktors.

3. Katalytische Destillationsstruktur nach Anspruch 1, in der der starre Behälter einen Hohlzylinder mit einer inneren Wand umfaßt, die sich im allgemeinen parallel zur zylindrischen Wand des Zylinders erstreckt und deren Enden geschlossen sind, um den Raum innerhalb des Zylinders in einen zentralen Hohlraum, der an beiden Enden offen ist, und einen zweiten, den zentralen Raum umgebenden und an beiden Enden geschlossenen Raum aufzuteilen, wobei die Katalysatorkomponente im zweiten geschlossenen Raum angeordnet ist, der zweite Raum Öffnungen in den Enden und Wänden für den Ein- und Austritt von Flüssigkeit und Dampf aus dem zweiten Raum aufweist und sowohl die Länge als auch der Durchmesser dieses Behälters wesentlich kleiner als die entsprechenden Abmessungen des Destillationskolonnenreaktors ist.

4. Katalytische Destillationsstruktur nach Anspruch 1, in der der starre Behälter einen an beiden Enden geschlossenen Hohlzylinder mit einer sich im allgemeinen parallel zur zylindrischen Wand des Zylinders erstreckenden inneren Wand umfaßt, die den Raum innerhalb des Zylinders in einen geschlossenen zentralen Raum und einen zweiten, diesen zentralen Raum umgebenden geschlossenen Raum teilt, wobei die Katalysatorkomponente in diesem zentralen Raum angeordnet ist und die Enden und Wände Öffnungen für den Durchtritt von Flüssigkeit und Dampf durch den zweiten Raum und Ein- und Austritt aus dem zentralen Raum aufweisen.

5. Katalytische Destillationsstruktur nach einem der Ansprüche 1 bis 4, in der die Öffnungen kreisförmige Mündungen in den Enden und der Wand oder den Wänden des starren Behälters umfassen.

6. Katalytische Destillationsstruktur nach einem der Ansprüche 1 bis 4, in der die Öffnungen kreisförmige Mündungen in den Enden und längs geschlitzte Mündungen in der Wand oder den Wänden des starren Behälters umfassen.

7. Katalytische Destillationsstruktur nach Anspruch 6, die weiterhin eine Längsrippe umfaßt, die sich radial von einer Seite jeder der geschlitzten Mündungen erstreckt.

8. Katalytische Destillationsstruktur nach einem der Ansprüche 1 bis 7, in der die Öffnungen kleiner als die Teilchen der Katalysatorkomponente sind.

9. Katalytische Destillationsstruktur nach einem der Ansprüche 1 bis 8, in der die Öffnungen mit einem porösen Material bedeckt sind.

10. Katalytische Destillationsstruktur nach einem der Ansprüche 1 bis 7, in der die Öffnungen größer als die Teilchen der Katalysatorkomponente sind und die Struktur außerdem eine poröse Auskleidung umfaßt, um die Teilchen im Behälter zurückzuhalten.

11. Katalytische Destillationsstruktur nach einem der Ansprüche 1 bis 10, in der die Katalysatorkapazität des starren Behälters zwischen 14,2 und 1818 ml (1/2 bis 64 Flüssigunzen) liegt.

Revendications

1. Structure de distillation catalytique utile comme matériau de garnissage dans un réacteur à colonne de distillation, comprenant un composant catalytique particulaire disposé dans un récipient rigide percé d'ouvertures pour permettre le libre passage de liquide et de vapeurs, les surfaces du récipient fournissant des surfaces de contact de distillation, ce récipient ayant un volume notablement inférieur à celui du réacteur à colonne de distillation.

2. Structure de distillation catalytique suivant la revendication 1, dans laquelle ce récipient rigide comprend un cylindre creux fermé aux deux extrémités et ayant des ouvertures dans les extrémités et la paroi pour permettre au liquide et à la vapeur d'entrer dans le récipient et d'en sortir, la longueur et le diamètre de ce cylindre creux étant tous deux notablement inférieurs aux dimensions correspondantes de ce réacteur à colonne de distillation.

3. Structure de distillation catalytique suivant la revendication 1, dans laquelle ce récipient rigide comprend un cylindre creux ayant une paroi intérieure se prolongeant de façon généralement parallèle à la paroi cylindrique du cylindre et ayant des extrémités fermées pour diviser l'espace à l'intérieur du cylindre en un espace central creux qui est ouvert aux deux extrémités et un second espace entourant l'espace central qui est fermé aux deux extrémités, ce composant catalytique étant disposé dans ce second espace fermé, ce second espace ayant des ouvertures dans les extrémités et la paroi pour permettre au liquide et à la vapeur d'entrer dans ce second espace et d'en sortir, la longueur et le diamètre de ce récipient étant tous deux notablement inférieurs aux dimensions correspondantes de ce réacteur à colonne de distillation.

4. Structure de distillation catalytique suivant la revendication 1, dans laquelle ce récipient rigide comprend un cylindre creux fermé aux deux extrémités et ayant une paroi intérieure se prolongeant de façon généralement parallèle à la paroi cylindrique du cylindre, divisant l'espace à l'intérieur du cylindre en un espace central creux et un second espace fermé entourant cet espace central, ce composant catalytique étant disposé dans cet espace central et ces extrémités et parois ayant des ouvertures pour permettre au liquide et à la vapeur de traverser ce second espace et d'entrer dans cet espace central et d'en sortir.

5. Structure de distillation catalytique suivant l'une quelconque des revendications 1 à 4, dans laquelle ces ouvertures comprennent des orifices circulaires dans les extrémités et la paroi ou les parois de ce récipient rigide.

6. Structure de distillation catalytique suivant l'une quelconque des revendications 1 à 4, dans laquelle ces ouvertures comprennent des orifices circulaires dans les extrémités et des fentes longitudinales dans la paroi ou les parois de ce récipient rigide.

7. Structure de distillation catalytique suivant la revendication 6, comprenant de plus une ailette longitudinale se prolongeant radialement à partir d'un côté de chaque orifice en forme de fente.

8. Structure de distillation catalytique suivant l'une quelconque des revendications 1 à 7, dans laquelle ces ouvertures sont plus petites que les particules de ce composant catalytique.

9. Structure de distillation catalytique suivant l'une quelconque des revendications 1 à 8, dans laquelle ces ouvertures sont recouvertes d'un matériau poreux.

10. Structure de distillation catalytique suivant l'une quelconque des revendications 1 à 7, dans laquelle ces ouvertures sont plus grandes que les particules de ce composant catalytique et comprennent de plus un revêtement poreux pour retenir ces particules à l'intérieur de ce récipient.

11. Structure de distillation catalytique suivant l'une quelconque des revendications 1 à 10, dans laquelle la capacité de catalyseur de ce récipient rigide est comprise entre 14,2 et 1818 ml (1/2 à 64 ounces fluides).

FIG. 2

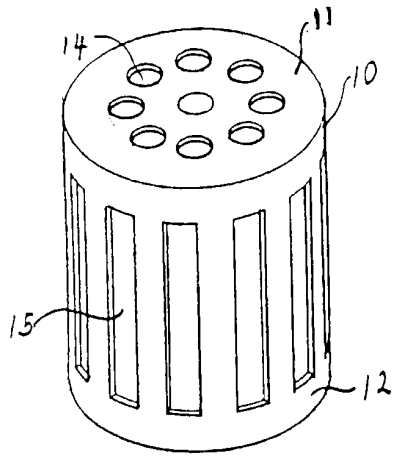


FIG. 1

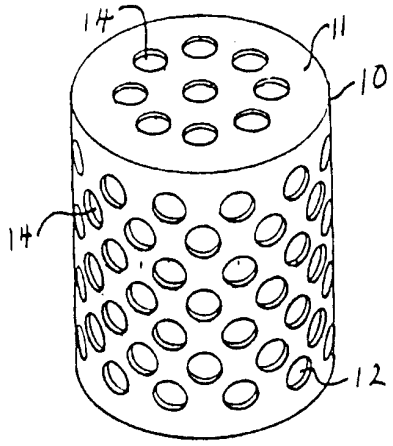
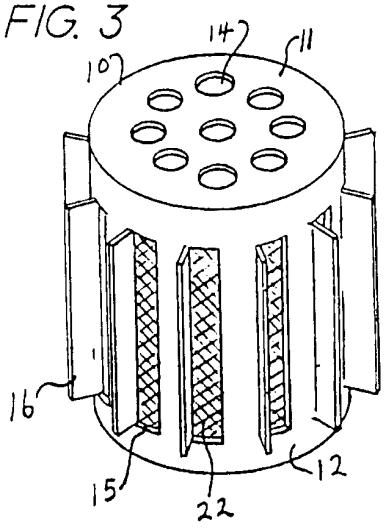


FIG. 3



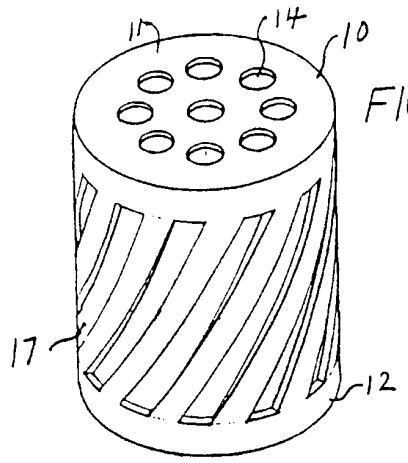


FIG. 4

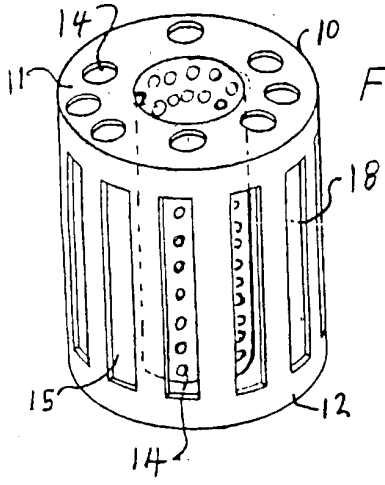


FIG. 6

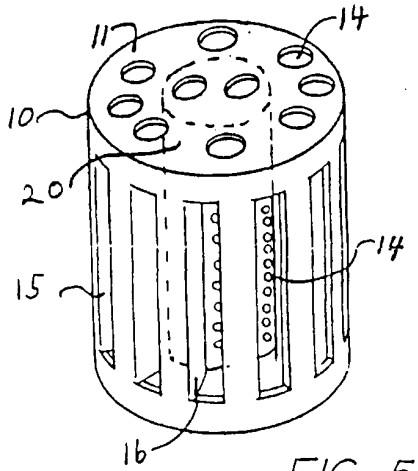


FIG. 5